80 J. Chem. Eng. Data 1981, 26, 80-84

(4) Boublik, T.; Fried, V.; Hala, E. H. "The Vapor Pressures of Pure Substance"; Elsevier: Amsterdam, 1973.
(5) Felsing, W. A.; Durban, S. A. *J. Am. Chem. Soc.* **1926**, *48*, 2885.
(6) Washburn, E. W., Ed. "International Critical Tables of Numerical Data, Physics, Chemistry and Technology"; McGraw-Hill: New York, 1928; Vol. 3.
(7) "Landolt-Bornstein Zahlenwerte und Funktionen 6. Auflage IV. Band Tecknik, 4. Teil Wärmetechnik Bestandteil cl, Absorption in Flüssigkeiten mit niedrigem Dampfdruck"; Springer-Verlag: Berlin, 1976.
(8) Lyckman, E. W.; Eckert, C. A.; Prausnitz, J. M. *Chem. Eng. Sci.* **1965**, *20*, 703.
(9) Prausnitz, J. M. "Molecular Thermodynamics of Fluid-Phase Equilibria"; Prentice-Hall: Englewood Cliffs, NJ, 1969.
(10) Rivas, O. Ph.D dissertation, University of California, Berkeley, CA, 1978.
(11) Dymond, J. H.; Smith, E. B. "The Virial Coefficients of Gases"; Clarendon Press: Oxford, 1969.
(12) Tsonopoulos, C. *AIChE J.* **1974**, *20*, 263.
(13) Hayden, J. G.; O'Connell, J. P. *Ind. Eng. Chem. Process Des. Dev.* **1975**, *14*, 209.
(14) O'Connell, J. P.; Prausnitz, J. M. *Ind. Eng. Chem. Process Des. Dev.* **1967**, *6*, 245.
(15) Fife, H. R.; Reid, E. W. *Ind. Eng. Chem.* **1930**, *22*, 513.
(16) Hirschfelder, J. O.; Curtiss, C. F.; Bird, R. B. "Molecular Theory of Gases and Liquids"; Wiley: New York, 1954.
(17) Katayama, T. *J. Chem. Eng. Jpn.* **1975**, *8*, 89.
(18) Vigdergauz, M.; Semkin, V. *J. Chromatogr.* **1971**, *58*, 95.

Received for review May 20, 1980. Accepted October 17, 1980. Acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. This research was also supported by grants from the National Science Foundation and the Deutsche Forschungsgemeinschaft.

Pressure Effects on Conductivity and Ionic Association of Some Monovalent Salts in Aprotic Dipolar Solvents

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The conductance of LiI, LiBr, and NaI in acetonitrile and of tetra-*n*-butylammonium iodide and tetra-*n*-butylammonium bromide in acetone and in 4-methyl-2-pentanone were measured as a function of pressure. Data are reported at 25 °C over a concentration range of 0.0001–0.03 M and at pressures up to 2–3 kbar. Analysis of these data using Justice's modification of the Fuoss–Onsager equation yields values of the limiting conductance and the association constants as a function of pressure. Both the limiting conductance values and the association constants decrease with increasing pressure, and from the latter values of the volume change on association are calculated.

Introduction

High pressure is an extremely powerful tool for the study of reaction mechanisms and kinetic solvent effects, by careful measurement of variations in the volume of activation (*1*, *2*). In order to make such studies on ionic reactions in dipolar aprotic solvents, the degree of dissociation as a function of pressure must be well-known, as most often only the dissociated ion is kinetically active (*3*, *4*). Conductance measurements yield both the association constant as well as information about the relative solvating ability of solvents for various ions. High-pressure determinations yield, as well as the association constant, the limiting conductance as a function of pressure, and the volume change for ion-pair formation.

The conductance of NaI, LiI, and LiBr was measured in acetonitrile. The conductance of tetra-*n*-butylammonium iodide (Bu_4NI) and tetra-*n*-butylammonium bromide (Bu_4NBr) was measured in acetone and in 4-methyl-2-pentanone. These combinations of salts and solvents were chosen for use in conjunction with a kinetic study of a halide-exchange reaction under pressure (*5*).

Experimental Section

A diagram of the high-pressure conductance cells that were used in this study is shown in Figure 1. The main body of each cell was Teflon, to resist pressure cycling, but the platinum plates were firmly supported in glass to minimize the variation in cell constant with pressure. The cells were attached to a mercury reservoir, and each contained ~40 mL of electrolyte and 20 mL of mercury. Two cells were used with cell constants of ~0.05 and 0.5. These cell constants were measured as a function of pressure by using the data of Fisher (*6*) and Fuoss (*7*) for KCl in water. The variation in cell constant to 3 kbar was much less than 1%.

The pressure system was essentially similar to that used in a previous study of this type (*8*); measured pressures are accurate to ±2 bar and temperatures to ±0.01 °C.

The chemicals used in this study were purified according to the procedure suggested by Perrin (*9*).

Lithium iodide from Mallinckrodt Chemical Works was recrystallized from acetone. The filtered lithium iodide solution was evaporated at room temperature under vacuum. The residual hydrated crystal was dried at 60 °C under vacuum for 2 h and then at 120 °C under high vacuum by using the Abderhalden drying apparatus.

Lithium bromide from Fisher Scientific Co. was recrystallized several times from water and then dried under high vacuum at room temperature, followed by drying at 100 °C.

Sodium iodide from Mallinckrodt Chemicals Works (purity 99.5%) was recrystallized from ethanol and dried for 12 h under vacuum at 70 °C.

$(Bu)_4NI$ was obtained from Eastman Kodak Co. and was dried for 24 h under strong vacuum at room temperature in the presence of P_2O_5. Solutions of $(Bu)_4NI$ were prepared by weight and checked by titration with $AgNO_3$ solutions. The determinations always agreed within 1%. $(Bu)_4NI$ solutions were shaken with starch solutions, and no color change due to I_2 was observed. Karl Fisher titrations showed no water.

$(Bu)_4NBr$ was obtained from Matheson Coleman and Bell. It was dried for 24 h under strong vacuum in the presence of P_2O_5. Solutions of $(Bu)_4NBr$ were prepared by titration with $AgNO_3$. Karl Fisher titrations showed no water.

Acetonitrile was Baker's analyzed reagent grade and was dried by shaking with Linde 4A molecular sieves and then stirred with calcium hydride until no further hydrogen was evolved. The acetonitrile was then fractionally distilled at a high reflex ratio.

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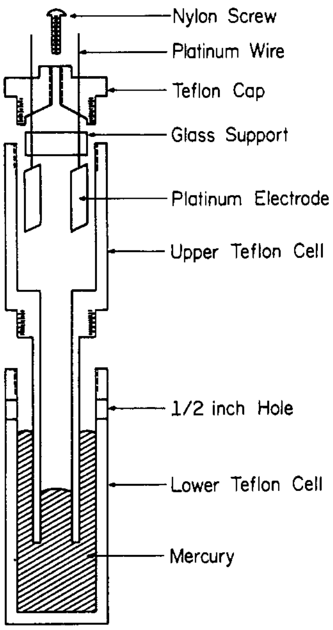

Figure 1. High-pressure conductance cell.

The specific conductance of the purified acetonitrile was 1.5 × 10^{-7} Ω^{-1} cm^{-1}.

Acetone was obtained from Fisher Scientific Co. and was purified by drying over molecular sieves and by subsequent distillation. Since water was considered the most harmful contaminant, the acetone was stored over molecular sieves. Acetone was tested by Karl Fisher titration for water and by gas chromatography for organics. No contaminants were found.

4-Methyl-2-pentanone was obtained from Aldrich Chemical Co. and was used without purification. It was tested by gas chromatography and by index of refraction. No contamination was found.

All electrolytic solutions were prepared by volume in a temperature bath using calibrated flasks. The concentration of the most concentrated solution was determined by titration with a standard $AgNO_3$ solution. All of the less concentrated solutions were prepared by dilution.

Further details of the experimental procedure are available elsewhere (*10*).

Results

Once the conductance of each of the solutions was measured at the desired pressures, the association constant was calculated at each pressure with the Fuoss–Onsager equation (*11*) as modified by Justice (*12*)

$$\Lambda = (\Lambda_0 + S(c\gamma)^{1/2} + Ec\gamma \log c\gamma + Jc\gamma + J_{3/2}(c\gamma)^{3/2})\gamma \qquad (1)$$

$$K_a = (1 - \gamma)/(c\gamma^2 f^2) \qquad (2)$$

Here S is the Onsager limiting slope, and the coefficients S, E, J, and $J_{3/2}$ are functions of Λ_0 and the dielectric constant, viscosity, and temperature of the solvent. In addition J and $J_{3/2}$ are functions of the critical approach distance for an ion pair. The viscosity of each solution has been corrected for ionic concentration by using the Jones–Dole viscosity equation (*13*, *14*). K_a is the association constant, and f is the mean ionic activity coefficient, calculated with Debye–Hückel theory.

To use eq 1 and 2 for systems under pressure, one must know the pressure dependence of the density, the dielectric constant, and the viscosity of our three solvents. The densities of acetone, acetonitrile, and 4-methyl-2-pentanone were measured by Bridgeman (*15*), Smith (*16*), and Andersen (*17*), respectively. Bridgeman (*18*) and DeZwann (*19*) measured the viscosity of acetone and acetonitrile, respectively. The pressure dependence on the viscosity of 4-methyl-2-pentanone was not available in the literature and was assumed to be the same as seen in acetone. The pressure dependence on the dielectric constant of acetone was measured by Hartmann, Neumann, and Rinck (*20*). Dielectric-constant data were not available for either acetonitrile or 4-methyl-2-pentanone. The pressure dependence on the dielectric constant of acetonitrile was assumed to be the same as seen in a similar compound, propionitrile (*21*). The pressure dependence of the dielectric constant of 4-methyl-2-pentanone was assumed to be the same as acetone.

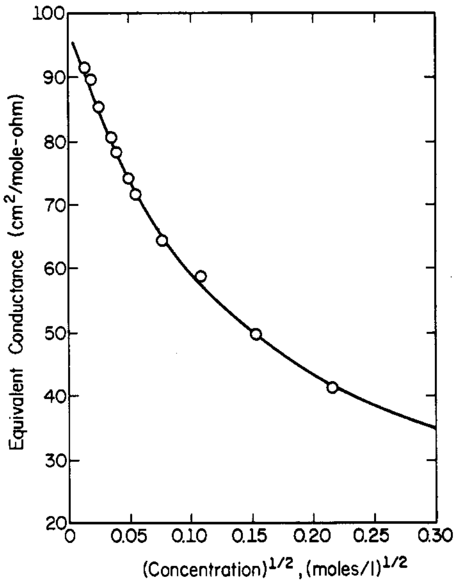

Figure 2. Typical data set for the equivalent conductance of tetrabutylammonium bromide in acetone. Data at 1725 bar, 25 °C.

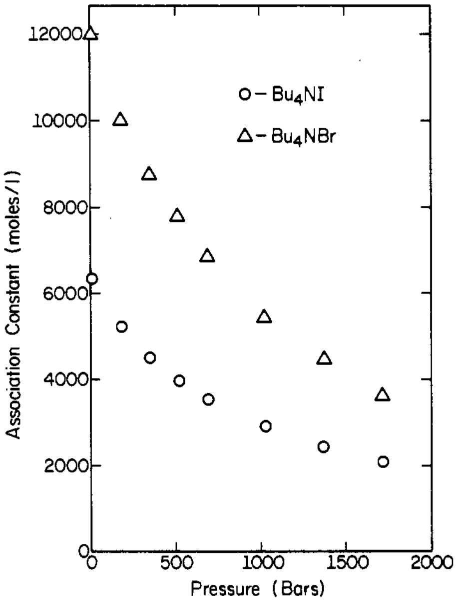

Figure 3. Association constant as a function of pressure for tetrabutylammonium iodide and tetrabutylammonium bromide in 4-methyl-2-pentanone at 25 °C.

The conductance data are listed in Table I. A typical data set is shown in Figure 2 along with the theoretical Fuoss–Onsager fit of those data.

Table II lists the calculated association constants and limiting equivalents conductances for all of the combinations of salt and solvent. The association constants in acetone and in 4-

Table I. Equivalent Conductance Data at 25.00 °C[a]

P	c	Λ	c	Λ	c	Λ	c	Λ
Bu_4NI in Acetone								
1	1.665	180.5	3.330	172.6	6.659	164.2	13.32	149.5
345	1.701	153.6	3.403	146.6	6.805	140.7	13.61	130.7
690	1.728	133.3	3.457	139.6	6.912	123.2	13.83	115.0
1035	1.750	118.4	3.500	114.2	6.998	110.2	14.00	103.2
1380	1.768	107.4	3.535	103.3	7.070	99.45	14.14	94.01
1725	1.783	96.52	3.566	93.32	7.132	89.97	14.27	84.90
2069	1.797	87.04	3.594	84.69	7.186	81.76	14.37	77.03
2759	1.820	72.77	3.640	73.35	7.279	68.95	14.56	65.18
1	16.84	146.3	26.64	135.6	33.68	130.3	66.60	108.1
345	17.21	127.1	27.22	118.8	34.42	114.2	68.06	96.53
690	17.48	111.7	27.65	105.4	34.96	101.6	69.13	86.82
1035	17.70	100.6	28.00	94.83	35.40	91.73	69.99	78.65
1380	17.88	91.36	28.23	87.02	35.76	83.76	70.71	71.56
1725	18.04	82.81	28.53	78.61	36.07	75.99	71.33	65.67
2069	18.17	75.34	28.75	71.70	36.35	68.88	71.87	60.12
2759	18.40	64.17	29.12	60.70	36.81	58.48	72.80	51.19
1	133.2	91.47	266.3	75.99	532.4	61.61		
345	136.1	83.22	272.1	68.98	544.1	57.20		
690	138.3	75.31	276.4	63.57	552.7	52.94		
1035	140.0	68.37	279.9	58.29	559.6	48.35		
1380	141.4	63.16	282.7	53.88	565.3	44.95		
1725	142.7	57.91	285.2	49.63	570.2	41.37		
2069	143.7	53.09	287.4	45.92	574.5	38.11		
2759	145.6	45.28	291.1	39.46	581.9	33.06		
Bu_4NBr in Acetone								
1	1.337	170.6	2.674	164.2	5.349	151.4	10.70	138.7
345	1.366	145.5	2.733	141.3	5.466	131.6	10.93	122.0
690	1.388	126.7	2.776	123.6	5.553	115.9	11.11	108.0
1035	1.405	113.0	2.810	110.4	5.621	104.1	11.25	97.59
1380	1.420	101.9	2.839	99.35	5.679	94.54	11.36	88.78
1725	1.432	91.83	2.864	89.96	5.729	85.73	11.46	80.98
2069	1.442	83.17	2.886	81.85	5.772	77.73	11.55	73.80
2759	1.461	69.82	2.923	68.84	5.847	65.53	11.70	62.33
1	13.36	133.1	21.39	127.3	26.71	117.2	53.42	100.3
345	13.65	117.1	21.86	109.1	27.29	104.4	54.59	91.10
690	13.87	104.6	22.20	97.87	27.73	94.22	55.45	82.83
1035	14.04	94.66	22.48	89.11	28.07	85.90	56.14	75.98
1380	14.18	86.49	22.71	81.58	28.36	79.01	56.71	70.28
1725	14.31	78.68	22.91	74.58	28.61	71.97	57.21	64.65
2069	14.42	71.63	23.08	68.12	28.82	65.66	57.65	59.30
2759	14.60	60.90	23.38	58.01	29.20	56.37	58.39	50.99
1	106.9	86.06	213.7	69.71	427.3	56.07		
345	109.2	80.15	218.4	65.50	436.7	53.29		
690	111.0	74.17	221.8	61.32	443.6	50.20		
1035	112.3	68.45	224.6	61.60	449.1	47.19		
1380	113.5	63.49	226.9	53.46	453.7	43.89		
1725	114.5	58.94	228.9	49.87	457.6	41.48		
2069	115.4	54.76	230.6	46.57	461.1	38.64		
2759	116.8	47.64	233.6	40.69	467.1	33.93		
Bu_4NI in 4-Methyl-2-pentanone								
1	0.1574	45.95	0.3149	47.70	0.6299	43.84	1.259	65.29
173	0.1608	40.08	0.3216	41.52	0.6433	38.87	1.286	59.20
345	0.1637	35.18	0.3274	36.21	0.6548	34.27	1.309	54.23
518	0.1662	31.37	0.3324	32.33	0.6648	30.65	1.329	49.75
690	0.1684	28.05	0.3368	28.79	0.6737	27.43	1.347	45.77
1035	0.1723	22.59	0.3446	23.16	0.6892	22.21	1.378	38.93
1380	0.1755	18.37	0.3511	18.80	0.7024	18.14	1.404	33.12
1725	0.1784	14.96	0.3569	15.46	0.7139	14.96	1.427	28.27
1	2.519	55.84	3.145	51.41	5.038	46.03	6.290	42.26
173	2.573	50.97	3.212	47.24	5.146	42.56	6.424	39.12
345	2.619	46.88	3.269	43.65	5.237	39.69	6.539	36.50
518	2.659	43.23	3.319	40.36	5.318	36.97	6.639	34.05
690	2.695	39.93	3.364	37.36	5.389	34.45	6.728	31.72
1035	2.757	34.19	3.441	32.18	5.513	29.93	6.883	37.66
1380	2.810	29.18	3.507	27.55	5.618	25.89	7.014	23.99
1725	2.855	25.13	3.564	23.77	5.710	22.49	7.129	20.92
1	12.58	34.15	25.16	27.23	50.34	22.97	100.6	18.19
173	12.85	31.89	25.70	25.55	51.41	21.89	102.8	17.29
345	13.08	29.93	26.15	24.09	52.33	20.73	104.6	16.43
518	13.28	28.10	26.55	22.70	53.13	19.63	106.2	15.57
690	13.46	26.32	26.91	21.41	53.85	18.53	107.6	14.71
1035	13.77	23.18	37.53	18.98	55.08	16.47	110.1	13.17
1380	14.03	20.23	28.05	16.73	56.13	14.62	112.2	11.70
1725	14.26	17.78	28.51	14.80	57.05	12.93	114.1	10.93

Table I (*Continued*)

P	c	Λ	c	Λ	c	Λ	c	Λ
$(Bu)_4NBr$ in 4-Methyl-2-pentanone								
1	0.2256	62.90	0.4513	55.15	0.9027	44.16	1.805	47.76
173	0.2305	55.66	0.4609	49.51	0.9220	38.80	1.844	44.15
345	0.2346	49.74	0.4692	44.57	0.9385	34.50	1.876	40.92
518	0.2382	44.73	0.4763	40.24	0.9528	30.88	1.905	38.07
690	0.2414	40.22	0.4827	36.31	0.9656	27.75	1.931	35.36
1035	0.2469	32.90	0.4938	29.82	0.9878	22.68	1.975	30.78
1380	0.2516	27.09	0.5033	24.56	1.0067	18.62	2.023	26.63
1725	0.2557	22.55	0.5115	20.44	1.0232	15.48	2.046	22.92
1	3.611	38.46	4.505	35.09	7.221	29.98	9.011	27.38
173	3.688	35.82	4.601	32.84	7.375	28.14	9.203	25.86
345	3.754	33.56	4.683	30.90	7.506	26.58	9.368	24.49
518	3.811	31.46	4.755	29.06	7.621	25.02	9.511	23.15
690	3.862	29.52	4.819	27.24	7.724	23.57	9.639	21.81
1035	3.951	25.28	4.929	24.02	7.901	20.93	9.860	19.45
1380	4.026	22.55	5.023	21.05	8.052	18.45	10.048	17.21
1725	4.092	19.74	5.106	18.47	8.184	16.26	10.213	15.22
1	18.03	21.78	36.04	16.30	72.10	13.88	144.2	11.01
173	18.41	20.74	36.81	15.51	73.63	13.29	147.2	10.63
345	18.74	19.74	37.47	14.81	74.95	12.67	149.9	10.19
518	19.03	18.78	38.04	14.10	76.10	12.09	152.3	9.737
690	19.28	17.81	38.55	13.41	77.12	11.53	154.2	9.305
1035	19.72	15.99	39.44	12.15	78.89	10.44	157.7	8.419
1380	20.10	14.24	40.19	10.91	80.39	9.427	160.8	7.601
1725	20.43	12.71	40.85	9.806	81.71	8.461	163.4	6.832
Lithium Bromide in Acetonitrile								
1	0.6600	170.1	1.378	167.0	2.810	162.3	7.361	151.7
173	0.6681	158.7	1.395	155.9	2.845	151.6	7.451	142.4
345	0.6787	148.4	1.417	146.1	2.890	142.1	7.569	133.8
690	0.6957	131.1	1.452	129.6	2.962	126.2	7.759	119.2
1035	0.7113	116.5	1.485	115.1	3.029	112.2	7.933	106.9
1552	0.7299	99.82	1.524	98.82	3.108	96.71	8.141	92.61
2069	0.7464	86.60	1.558	85.63	3.178	84.01	8.325	80.63
1	14.83	140.2	29.67	123.5	74.00	96.88	148.7	76.16
173	15.01	132.1	30.03	117.3	74.91	92.98	150.5	73.46
345	15.25	124.5	30.50	111.0	76.09	88.65	152.9	70.56
690	15.63	111.6	31.27	100.6	77.99	81.39	156.7	65.41
1035	15.98	100.5	31.97	91.42	79.75	74.48	160.2	60.39
1552	16.40	87.10	32.81	79.98	81.84	66.10	164.4	54.25
2069	16.77	76.18	33.55	70.53	83.69	59.11	168.1	48.74
Lithium Iodide in Acetonitrile								
1	1.384	175.6	3.696	172.3	7.451	168.4		
173	1.401	163.1	3.742	159.5	7.542	157.3		
345	1.423	151.6	3.201	148.8	7.661	146.5		
690	1.459	132.9	3.896	131.2	7.853	129.5		
1035	1.492	117.7	3.984	116.3	8.029	114.8		
1552	1.531	100.2	4.088	99.50	8.240	98.21		
2633	1.565	86.37	4.180	85.77	8.426	84.67		
1	19.28	160.5	43.53	150.0	79.25	139.5		
173	19.52	150.0	44.07	140.7	80.22	131.4		
345	19.82	140.3	44.76	131.9	81.49	123.1		
690	20.32	124.2	45.88	117.1	83.53	109.9		
1035	20.78	110.3	46.92	104.6	85.41	98.01		
1552	21.32	94.60	48.14	90.06	87.64	84.67		
2633	21.80	81.95	49.23	77.94	89.62	73.82		
Sodium Iodide in Acetonitrile								
1	1.241	185.3	3.806	180.3	7.950	176.5		
173	1.256	172.3	3.853	168.3	8.048	164.7		
345	1.276	160.0	3.913	156.9	8.175	153.7		
690	1.308	140.0	4.011	137.8	8.380	135.0		
1035	1.337	124.0	4.102	122.1	8.568	119.6		
1552	1.372	105.4	4.209	103.9	8.792	101.8		
2069	1.403	90.32	4.304	89.82	8.991	87.70		
1	22.78	166.5	60.78	152.2	120.1	135.5		
173	23.06	155.2	61.53	143.6	121.6	127.8		
345	23.43	145.2	62.50	134.9	123.5	120.5		
690	24.01	128.5	64.07	119.6	126.6	107.6		
1035	24.55	114.5	65.51	106.2	129.4	96.24		
1552	25.20	97.76	67.22	90.36	132.8	83.03		
2069	25.76	83.93	68.74	78.72	135.8	72.23		

[a] P = Pressure, bar absolute. Λ = Equivalent conductance, mho cm^2/mol. c = Concentration, 10^4(mol/L).

methyl-2-pentanone are accurate to within 3%. The association constants in acetonitrile are less accurate. The uncertainty in the association constants is due mainly to uncertainty in the concentrations of the most dilute electrolyte solutions.

Discussion

In a general way, the conductance data in Table I can be summarized by saying that conductance decreases with pres-

Table II. Limiting Conductance, Association Constants, and Volume of Association at 25 °C

	press bar	limiting conductance, mho cm^2/mol	association constant, mol/L	ΔV_0, cm^3/mol
Bu$_4$NI in acetone	1	198	398	14.0
	345	167	309	
	690	144	267	
	1035	127	234	
	1380	115	217	
	1725	103	197	
	2069	93.1	181	
	2759	78.8	167	
Bu$_4$NBr in acetone	1	185	469	17.3
	345	156	354	
	690	134	279	
	1035	118	224	
	1380	107	209	
	1725	96.5	200	
	2069	87.0	167	
	2759	72.8	136	
Bu$_4$NI in 4-methyl-2-pentanone	1	96.4	6190	23.8
	173	84.0	5098	23.8
	345	74.8	4370	
	518	66.9	3836	
	690	60.3	3396	
	1035	49.7	2753	
	1380	41.2	2295	
	1725	34.5	1940	
Bu$_4$NBr in 4-methyl-2-pentanone	1	93.1	11860	21.5
	173	81.9	9861	
	345	73.5	8607	
	518	66.3	7656	
	690	59.6	6707	
	1035	49.0	5300	
	1380	40.5	43.21	
	1725	33.4	3483	
LiBr in acetonitrile	1	174.5	163.1	14.8
	173	162.5	146.6	
	345	151.9	134.6	
	690	134.2	115.1	
	1035	119.0	94.5	
	1552	102.0	80.19	
	2069	88.4	69.0	
LiI in acetonitrile	1	180.2	23.4	24.0
	173	167.3	20.5	
	345	155.6	19.1	
	690	136.8	12.7	
	1035	121.0	9.33	
	1552	103.1	6.03	
	2069	88.9	4.21	
NaI in acetonitrile	1	189.5	27.6	33.4
	173	176.3	26.7	
	345	164.0	22.4	
	690	143.6	16.0	
	1035	126.8	10.5	
	1552	107.7	7.99	
	2069	92.8	8.96	

sure for these systems. There are two effects working in opposition to each other to produce this trend. First the viscosity of the solution increases dramatically with pressure. It more than doubles over the pressure range of interest. Second, the association constant goes down with pressure. This of course does not affect the low-concentration data, but it does tend to increase the conductance of a solution relative to its conductance at a lower pressure for the high-concentration solutions. The trend due to the change in association constant vs. pressure is never large enough to overcome the viscosity trend for the solution concentrations used in this study, and the conductivity always decreases with pressure.

Figure 3 demonstrates the pressure dependence of the association constants for typical systems. The association constants for all of the systems decrease with pressure. This means that, as pressure is applied to a system, the separated ions are becoming more stable with respect to the ion pair. This trend is due to the increase in dielectric constant with pressure for the solvents. The dielectric constant increases by 25% over the pressure range of interest. The solvent effects on the association constants also can be roughly correlated with the dielectric constant of the solvent. This trend is as one would expect. The activity of the ions in general goes down with increasing dielectric constant. The behavior of the ion pair is not important in explaining these phenomena qualitatively.

Volume changes for the association process can of course be evaluated from the pressure dependence of the association constants

$$\Delta V_0 = -RT(\partial \ln K_a/\partial P)_T \qquad (3)$$

The resulting volume changes range from 14 to 33 cm^3/mol, and they are listed in Table II.

Literature Cited

(1) Eckert, C. A. *Annu. Rev. Phys. Chem.* **1972**, *23*, 239.
(2) McCabe, J. R.; Eckert, C. A. *Acc. Chem. Res.* **1974**, *7*, 251.
(3) Evans, C. C.; Sugden, S. *J. Chem. Phys.* **1948**, *45*, 147.
(4) Winstein, S.; Savedoff, L. G.; Smith, S.; Stevens, I. D. R.; Gall, J. G. *Tetrahedron Lett.* **1960**, *9*, 24.
(5) Glugla, P. G.; Byon, J. H.; Eckert, C. A. "High Pressure Studies of Solvent Effects on a Halide Exchange Reaction"; *AIRAPT Conf.*, [*Proc.*], *6th*, 399 **1979**.
(6) Fisher, F. H. *J. Phys. Chem.* **1962**, *66*, 1607.
(7) Lind, J. E., Jr.; Zwolenik, J. J.; Fuoss, R. M. *J. Am. Chem. Soc.* **1959**, *81*, 1557.
(8) Sawin, S. P.; Eckert, C. A. *J. Chem. Eng. Data* **1971**, *16*, 476.
(9) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. "Purification of Latoratory Chemicals"; Pergamon: London, 1966.
(10) Glugla, P. G. Ph.D. Thesis, University of Illinois, Urbana, 1978.
(11) Fuoss, R. M.; Accascina, F. "Electrolytic Conductance"; Interscience: New York, 1959; Chapter XVII, pp 225–47.
(12) Burg. R.; Justice, M. G.; Justice, J. C. *C. R. Hebd. Seances Acad. Sci.* **1969**, *268*, 67.
(13) Fuoss, R. M. *J. Am. Chem. Soc.* **1957**, *79*, 3301.
(14) Jones, G.; Dole, N. *J. Am. Chem. Soc.* **1929**, *51*, 2950.
(15) Bridgman, P. W. *Proc. Am. Acad. Arts. Sci.* **1913**, *49*, 60.
(16) Smith, J. S. Ph.D. Thesis, University of Illinois, Urbana, 1975.
(17) Anderson, G. R. *Ark. Kemi* **1963**, *20*, 513.
(18) Bridgman, P. W. *Proc. Am. Acad. Arts Sci.* **1926**, *61*, 67.
(19) DeZwann, J.; Jonas, J., University of Illinois, personal communication, 1973.
(20) Hartmann, H.; Newman, A.; Rinck, G., *Z. Phys. Chem.* (*Frankfurt am Main*) **1965**, *44*, 218.
(21) Hartmann, H.; Schmidt, A. P. *Ber. Bunsenges. Phys. Chem.* **1968**, *72*, 875.

Received for review June 26, 1980. Accepted October 24, 1980. The financial support of the National Science Foundation is gratefully acknowledged.